

Vibrational Spectroscopy

Christian Hill

Remote Sensing Gone Wrong

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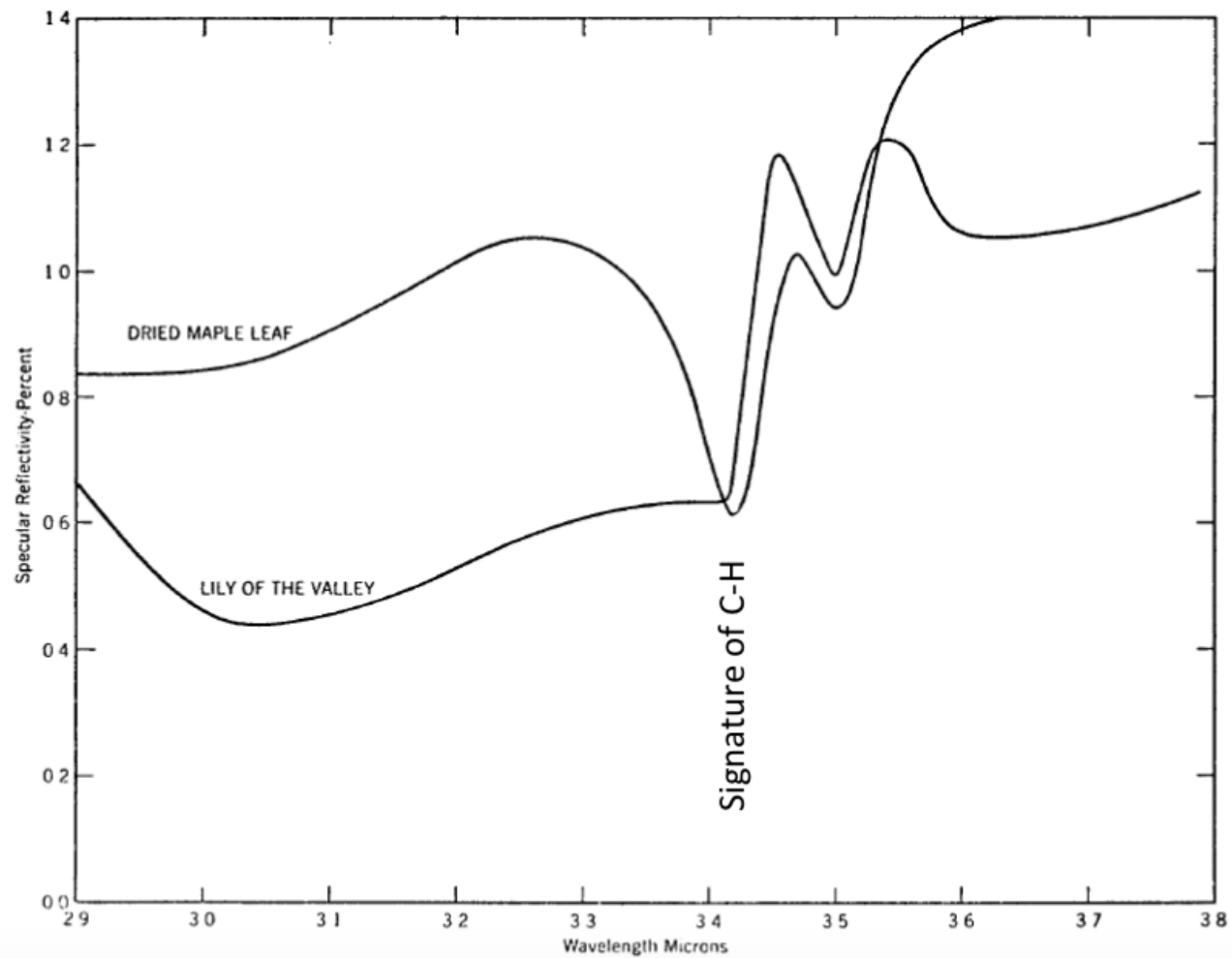
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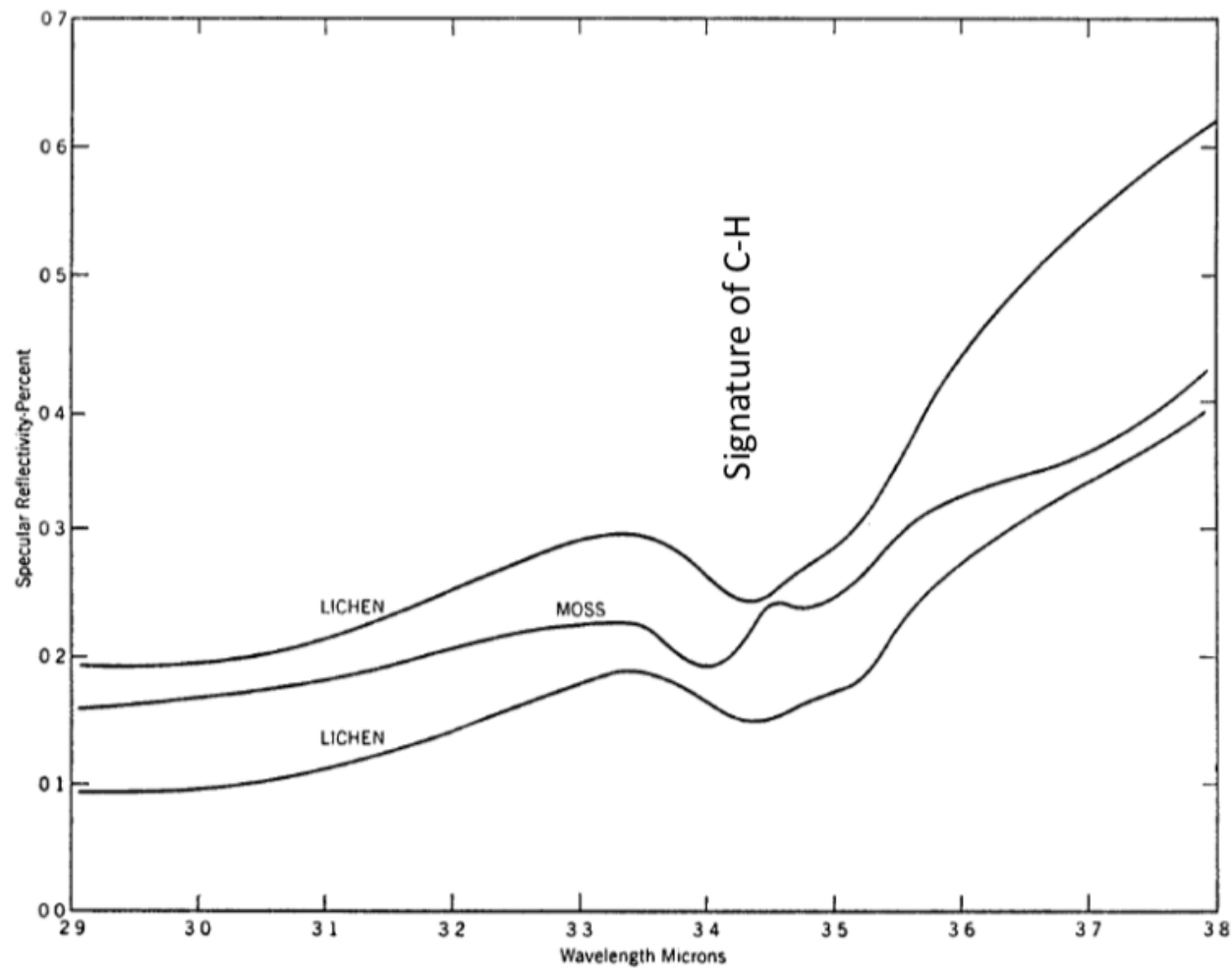
SPECTROSCOPIC EVIDENCE FOR VEGETATION ON MARS

WILLIAM M. SINTON
Smithsonian Astrophysical Observatory
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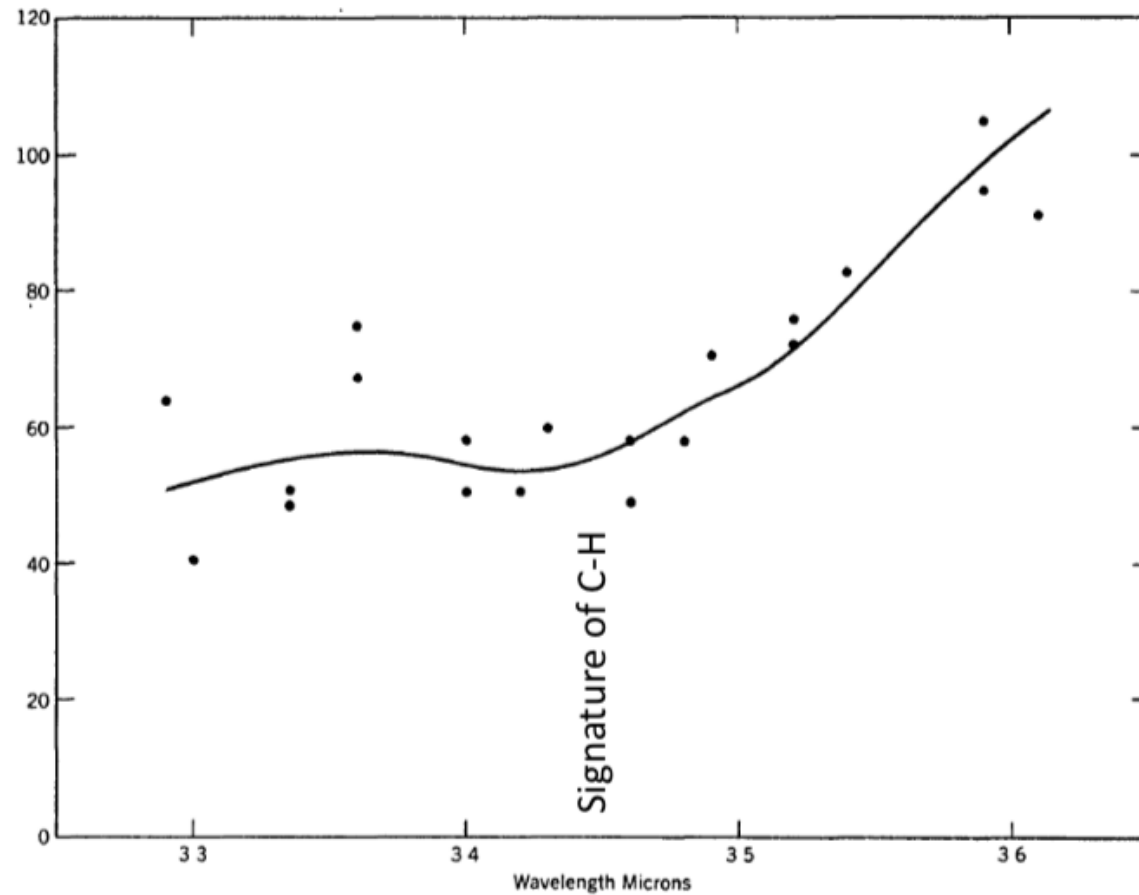
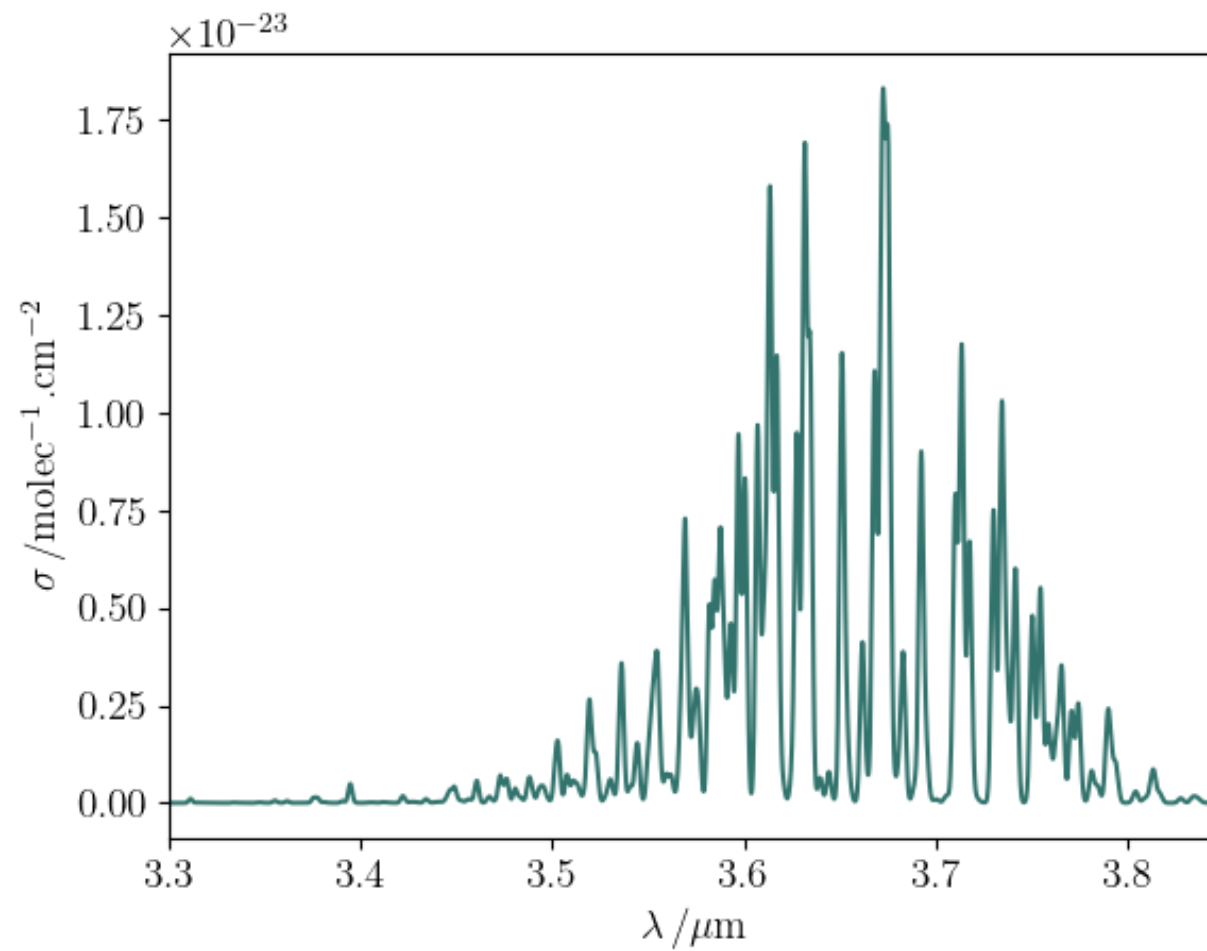


FIG. 3.—Observations of the spectrum of Mars obtained on four nights and after division by the solar spectrum (*solid curve* of Fig. 2).

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The Vibrational Hamiltonian

$$\nabla_R^2 S + \frac{2\mu}{\hbar^2} \left[E_{n,m} - V_n(R) - \frac{\hbar^2}{2\mu R^2} J(J+1) \right] S = 0$$

For the non-rotating molecule ($J = 0$):

$$\frac{1}{R^2} \frac{d}{dR} \left(R^2 \frac{dS}{dR} \right) + \frac{2\mu}{\hbar^2} [E_{n,m} - V_n(R)] S = 0$$

$V_n(R)$ is in general a complex function that depends on the electronic wavefunction, but for small displacements from R_e :

$$V_n(R) = V_n(R_e) + \frac{dV_n}{dR} (R - R_e) + \frac{1}{2} \frac{d^2 V_n}{dR^2} (R - R_e)^2 + \dots$$

The Vibrational Hamiltonian

$$V_n(R) = V_n(R_e) + \frac{dV_n}{dR}(R - R_e) + \frac{1}{2} \frac{d^2V_n}{dR^2}(R - R_e)^2 + \dots$$

We can choose the first term to be zero.

The second term *is* zero.

Defining the *bond force constant*,

$$k = \left. \frac{d^2V_n}{dR^2} \right|_{R_e}$$

we get $V_n(R) \approx \frac{1}{2}k(R - R_e)^2$

(the parabolic potential used earlier).

The Vibrational Hamiltonian

The resulting Schrödinger equation,

$$\frac{1}{R^2} \frac{d}{dR} \left(R^2 \frac{dS}{dR} \right) + \frac{2\mu}{\hbar^2} \left[E - \frac{1}{2} k (R - R_e)^2 \right] S = 0$$

can be solved exactly. Substitute $S(R) = \psi(x)/(x + R_e)$, where $x = R - R_e$ is the displacement of the nuclei from equilibrium to get:

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + \frac{1}{2} k x^2 \psi = E \psi.$$

Harmonic motion with frequency $\omega = \sqrt{k/\mu}$.

The Vibrational Hamiltonian: Non-dimensionalization

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi.$$

There is a characteristic length that we can scale x by: $\alpha = \hbar^p \mu^q k^r$ where the dimensions, $[\hbar] = [ML^2T^{-1}]$, $[\mu] = [M]$ and $[k] = [MT^{-2}]$.

Since $[\alpha] = [L]$ we must have

$$L : 1 = 2p$$

$$M : 0 = p + q + r$$

$$T : 0 = -p - 2r$$

and hence $p = \frac{1}{2}$, $q = -\frac{1}{4}$ and $r = -\frac{1}{4}$:

$$\alpha = \left(\frac{\hbar^2}{\mu k} \right)^{1/4}$$

The Vibrational Hamiltonian: Non-dimensionalization

With the new coordinate, $q = x/\alpha = (\mu k/\hbar^2)^{1/4}x$ the Schrödinger equation is:

$$-\frac{1}{2} \frac{d^2\psi}{dq^2} - \frac{1}{2}q^2 = \frac{E}{\hbar\omega} \psi$$

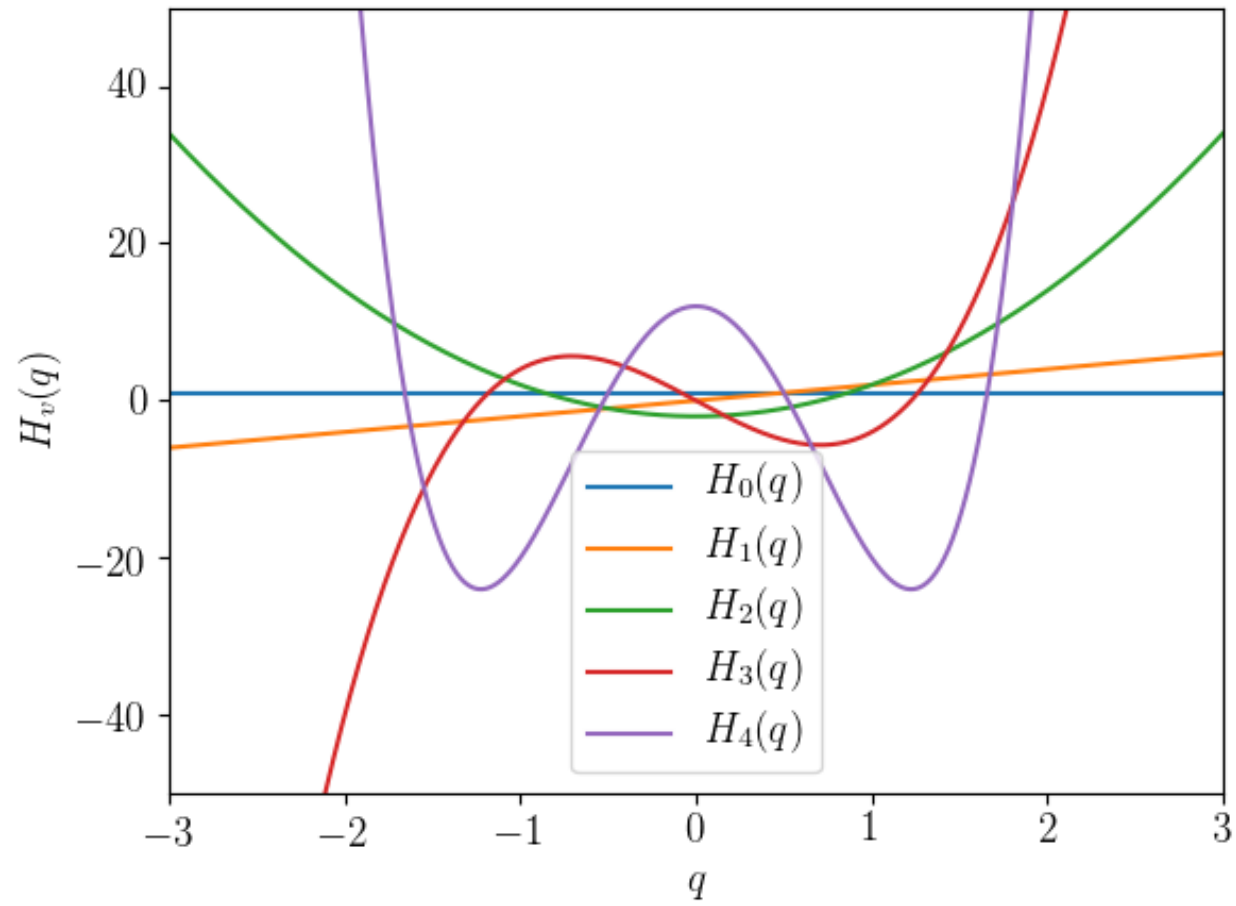
where $\omega = \sqrt{k/\mu}$ and its solutions are:

$$\psi(q) = N_v H_v(q) \exp(-q^2/2),$$

where $H_v(q)$ are *Hermite polynomials* and N_v is a normalization constant. The energy,

$$E_v = \hbar\omega(v + \frac{1}{2}) \quad \text{for } v = 0, 1, 2, \dots$$

Hermite Polynomials



Hermite Polynomials

- Definition:

$$H_v(q) = (-1)^v e^{q^2} \frac{d^v}{dq^v} \left(e^{-q^2} \right).$$

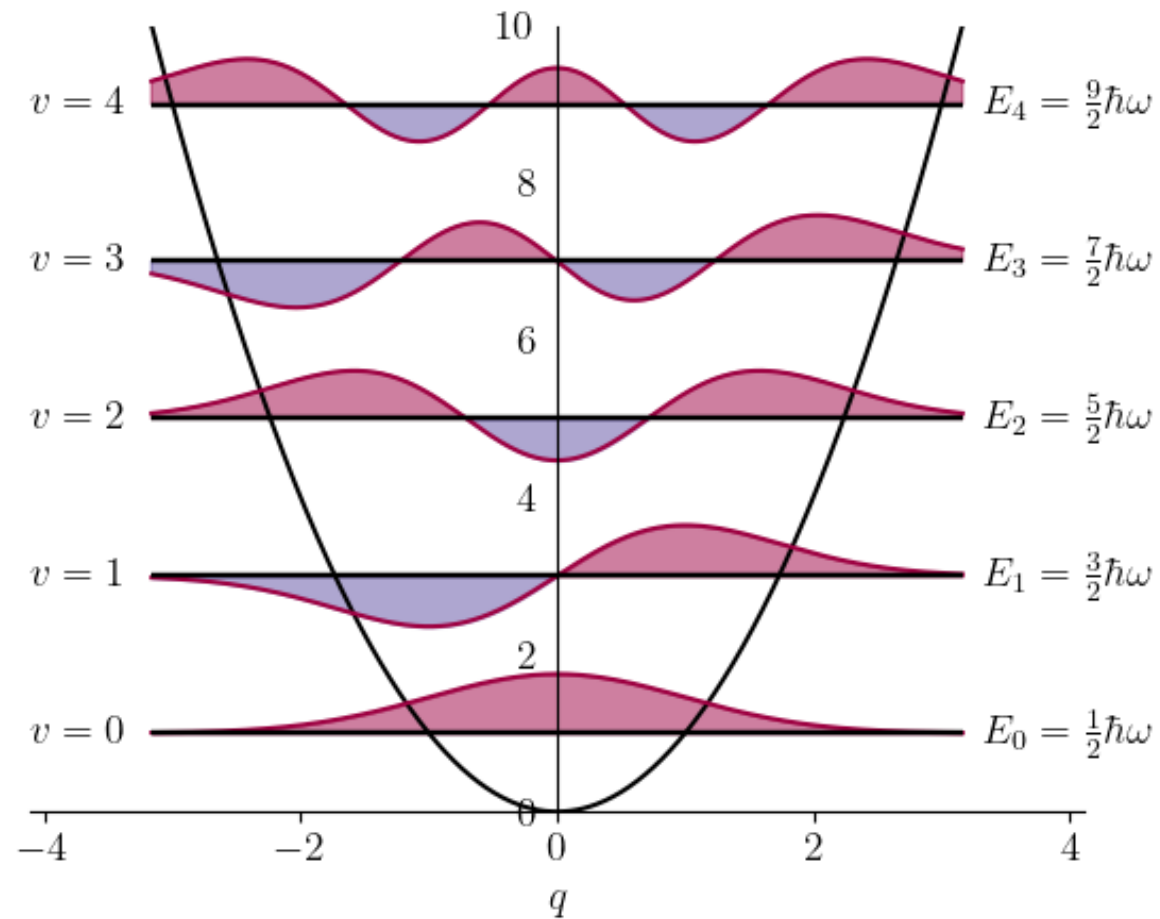
- Orthogonality with respect to weight function e^{-q^2} :

$$\int_{-\infty}^{\infty} H_m(q) H_n(q) e^{-q^2} dq = \sqrt{\pi} 2^n n! \delta_{nm}.$$

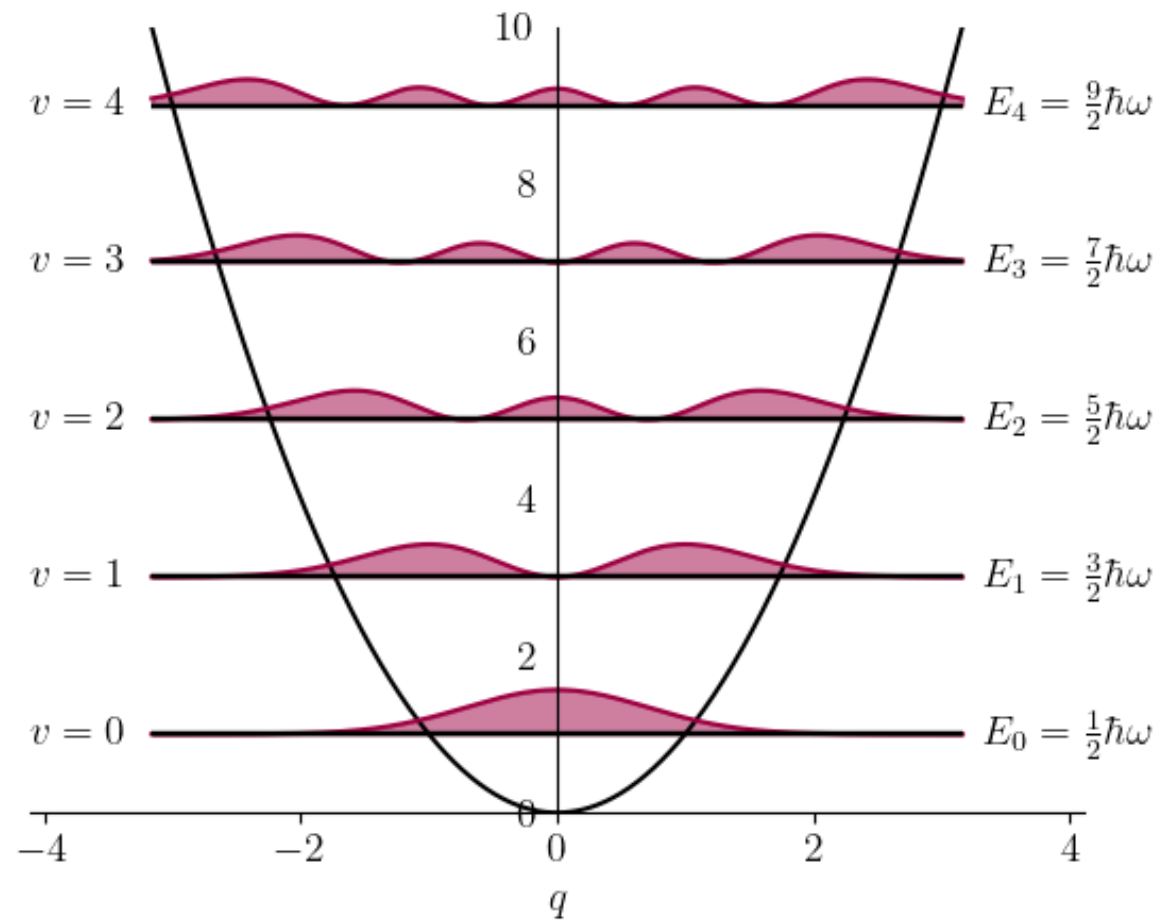
- Recursion:

$$H_{n+1}(q) = 2qH_n(q) - 2nH_{n-1}(q).$$

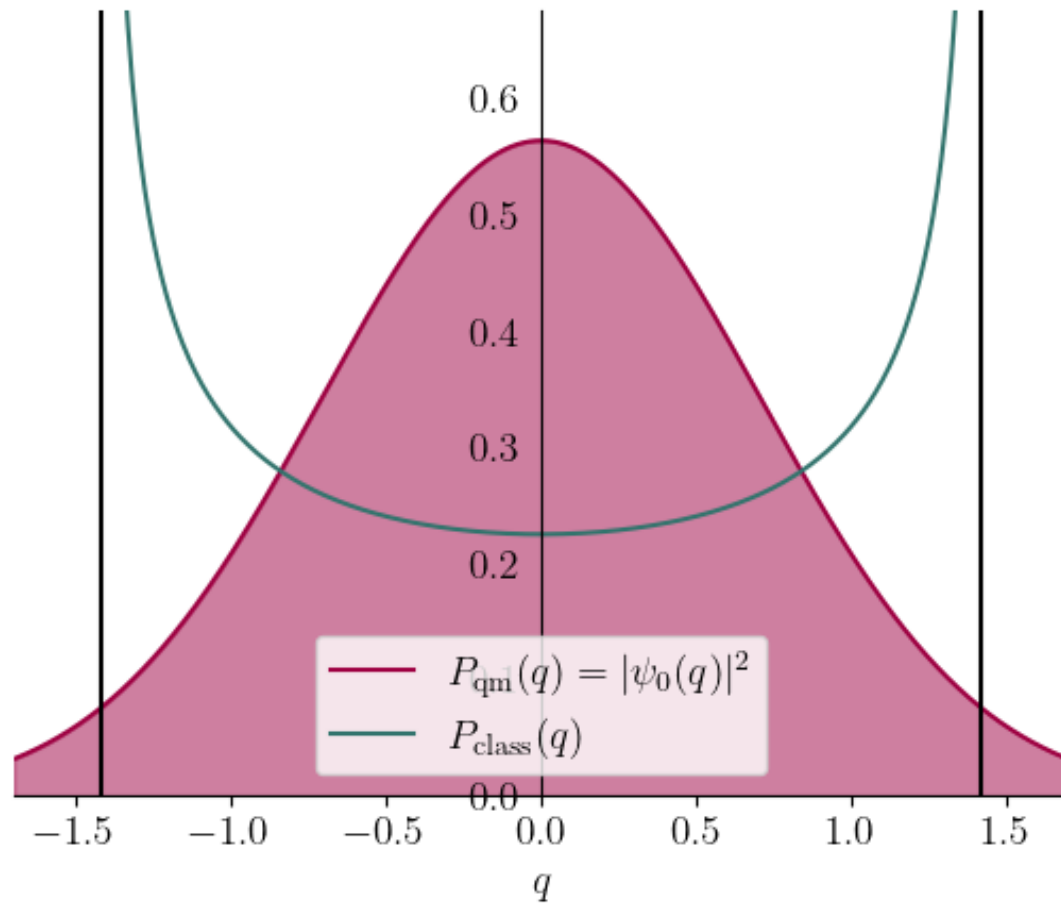
Harmonic Oscillator Wavefunctions



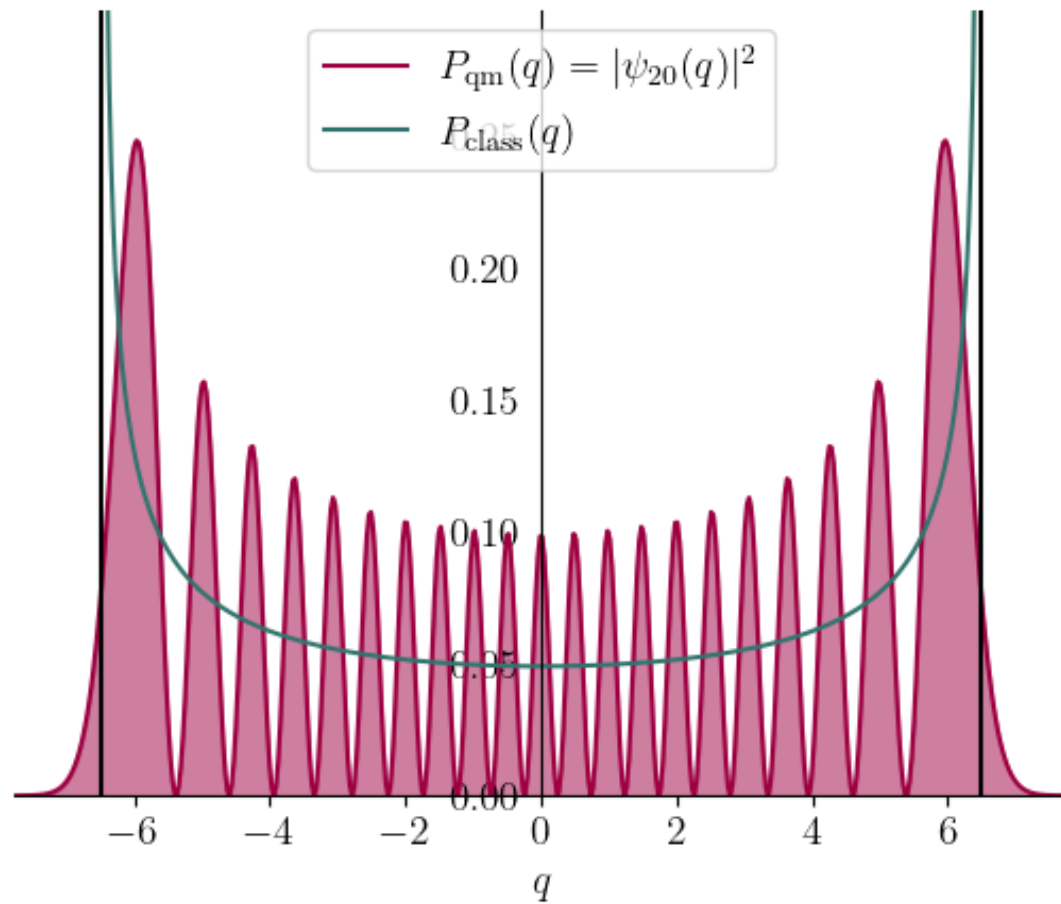
Harmonic Oscillator Probabilities



Harmonic Oscillator Probabilities



Harmonic Oscillator Probabilities



Vibrational Transitions

- The transition probability from one vibrational state, v'' to another, v' , is the square of the *transition dipole moment*:

$$M_{v'v''} = \int_{-\infty}^{\infty} \psi_{v'}^* \hat{\mu}(q) \psi_{v''} \, dq.$$

- The dipole moment operator is a complex function of q but may be expanded in a Taylor series:

$$\hat{\mu} = \mu_0 + \left. \frac{d\mu}{dq} \right|_0 q + \dots$$

- Therefore,

$$M_{v'v''} \approx \mu_0 \int_{-\infty}^{\infty} \psi_{v'}^* \psi_{v''} \, dq + \left. \frac{d\mu}{dq} \right|_0 \int_{-\infty}^{\infty} \psi_{v'}^* \cdot q \cdot \psi_{v''} \, dq$$

Vibrational Transitions

$$M_{v'v''} = \mu_0 \int_{-\infty}^{\infty} \psi_{v'}^* \psi_{v''} dq + \left. \frac{d\mu}{dq} \right|_0 \int_{-\infty}^{\infty} \psi_{v'}^* \cdot q \cdot \psi_{v''} dq$$

The first term here is zero by orthogonality of the Hermite polynomials, leaving

$$M_{v'v''} = \left. \frac{d\mu}{dq} \right|_0 N_{v''} N_{v'} \int_{-\infty}^{\infty} e^{-q^2} H_{v''}(q) q H_{v'} dq.$$

Using the recursion relation

$$H_{n+1}(q) = 2qH_n(q) - 2nH_{n-1}(q):$$

$$M_{v'v''} = \left. \frac{d\mu}{dq} \right|_0 N_{v''} N_{v'} \int_{-\infty}^{\infty} e^{-q^2} \left[\frac{1}{2} H_{v''+1}(q) + v'' H_{v''-1}(q) \right] H_{v'}(q) dq.$$

Vibrational Transitions: Selection Rules

$$M_{v'v''} = \left. \frac{d\mu}{dq} \right|_0 N_{v''} N_{v'} \int_{-\infty}^{\infty} e^{-q^2} \left[\frac{1}{2} H_{v''+1}(q) + v'' H_{v''-1}(q) \right] H_{v'}(q) dq.$$

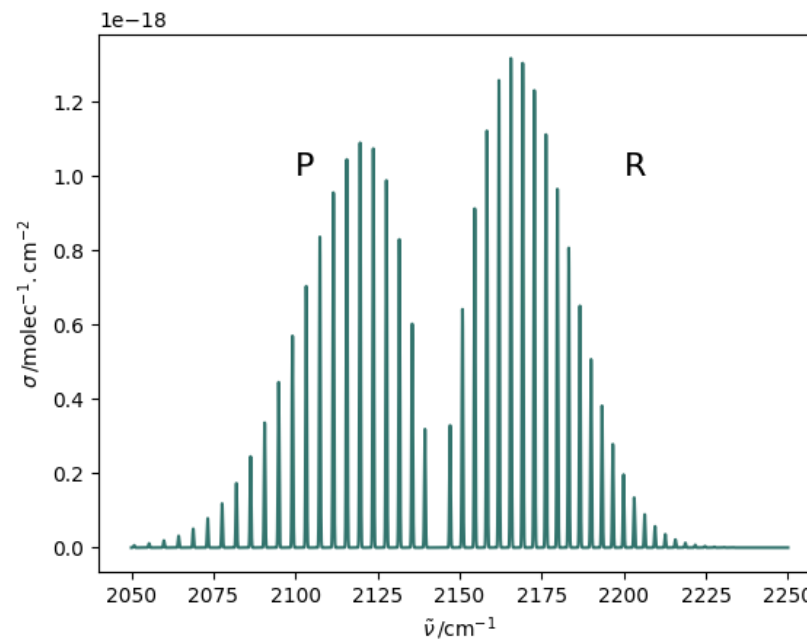
- *Gross selection rule:*

$$\left. \frac{d\mu}{dq} \right|_0 \neq 0$$

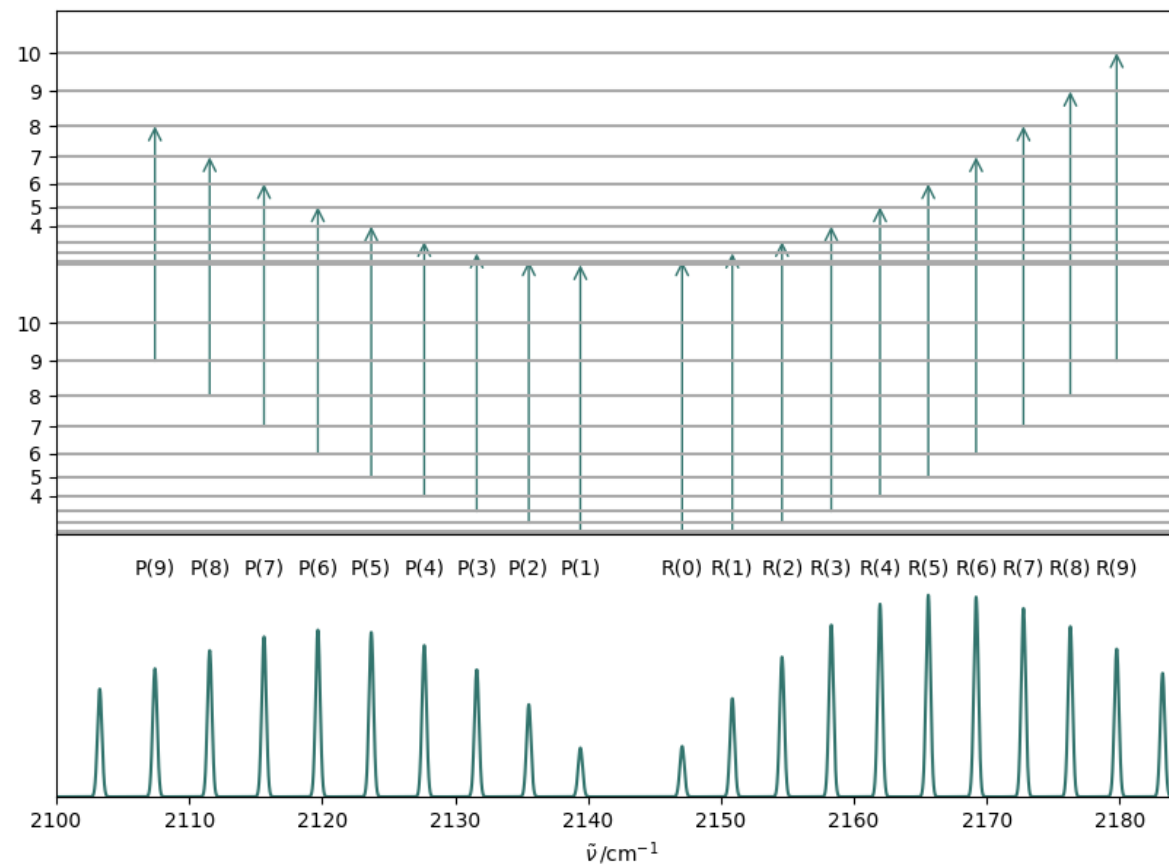
- $\Delta v = v' - v'' = \pm 1$
- NB homonuclear diatomics (e.g. H_2) do not have an (electric-dipole allowed) vibrational spectrum.

Rovibrational Transitions

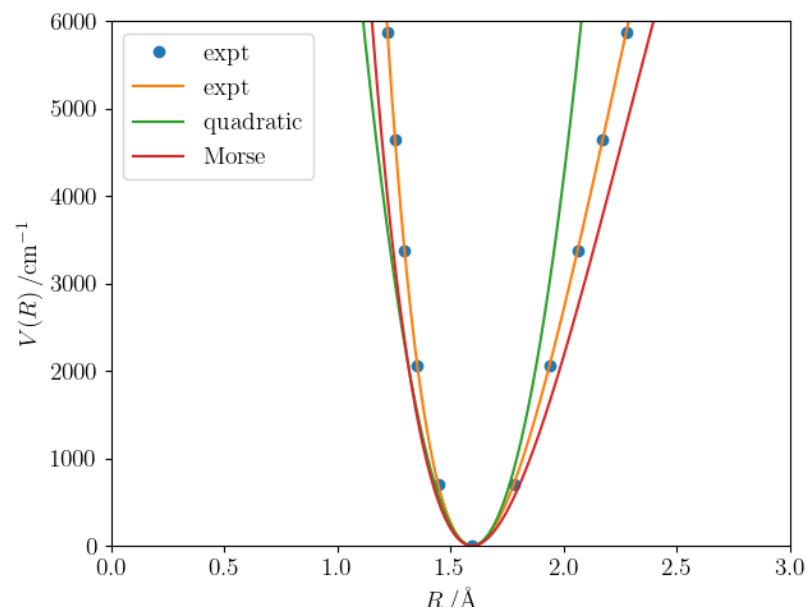
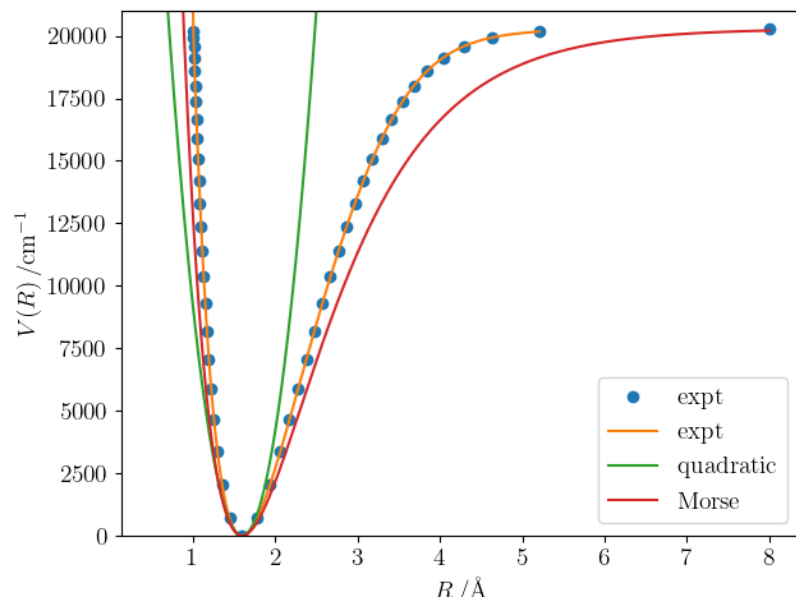
- Further selection rule on J : $\Delta J = \pm 1$
- P ($\Delta J = -1$) and R ($\Delta J = +1$) branches
- e.g. CO “fundamental” band: $v = 1 \leftarrow 0$



Rovibrational Transitions



Anharmonicity



- Real molecules dissociate
- Transitions with $\Delta v = \pm 2, \pm 3, \dots$ are (weakly) allowed
- $v = 0 \rightarrow 2, v = 0 \rightarrow 3$ overtones

Vibration-Rotation Interaction

When a molecule vibrates its moment of inertia, $I = \mu R^2$ changes

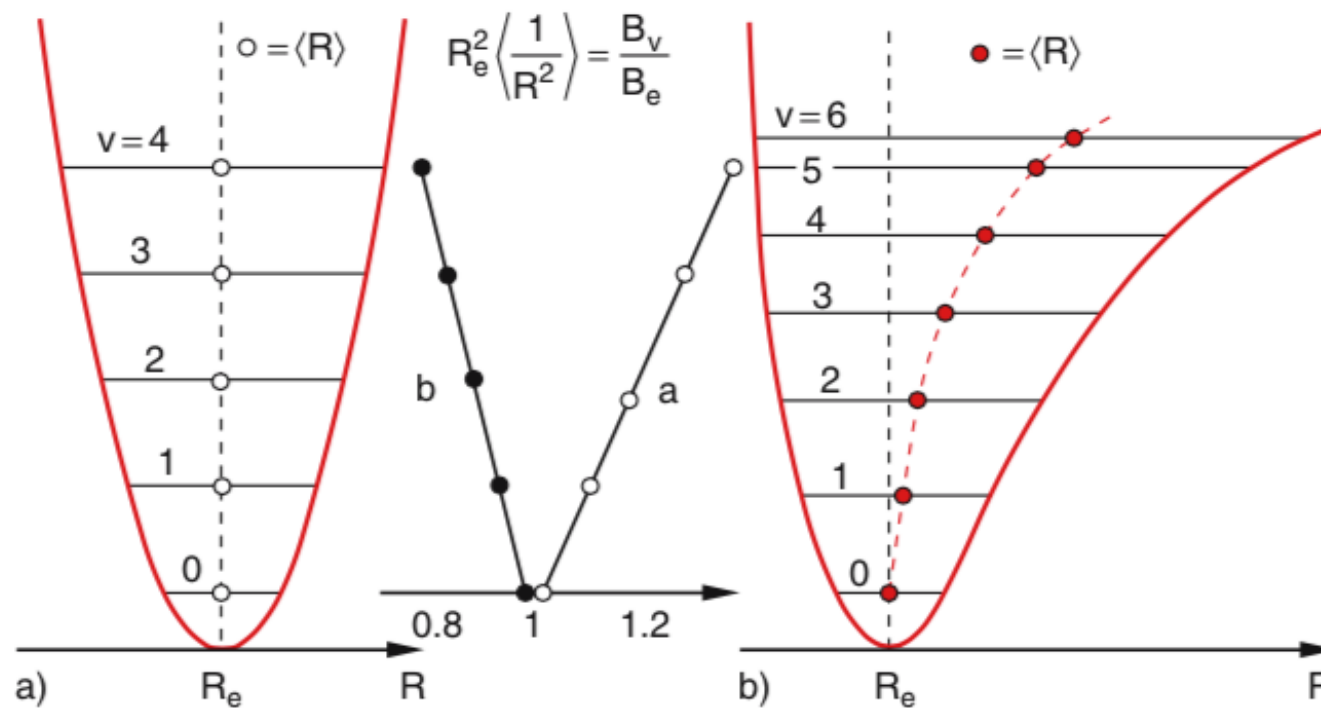
- The vibrational frequency is typically 10 – 100× faster than the rotational frequency
- Calculate the rotational energy using a time-average over a vibrational period:

$$\langle E_{\text{rot}}(J; \nu) \rangle = \frac{\hbar^2 J(J+1)}{2\mu} \left\langle \frac{1}{R^2} \right\rangle$$

where

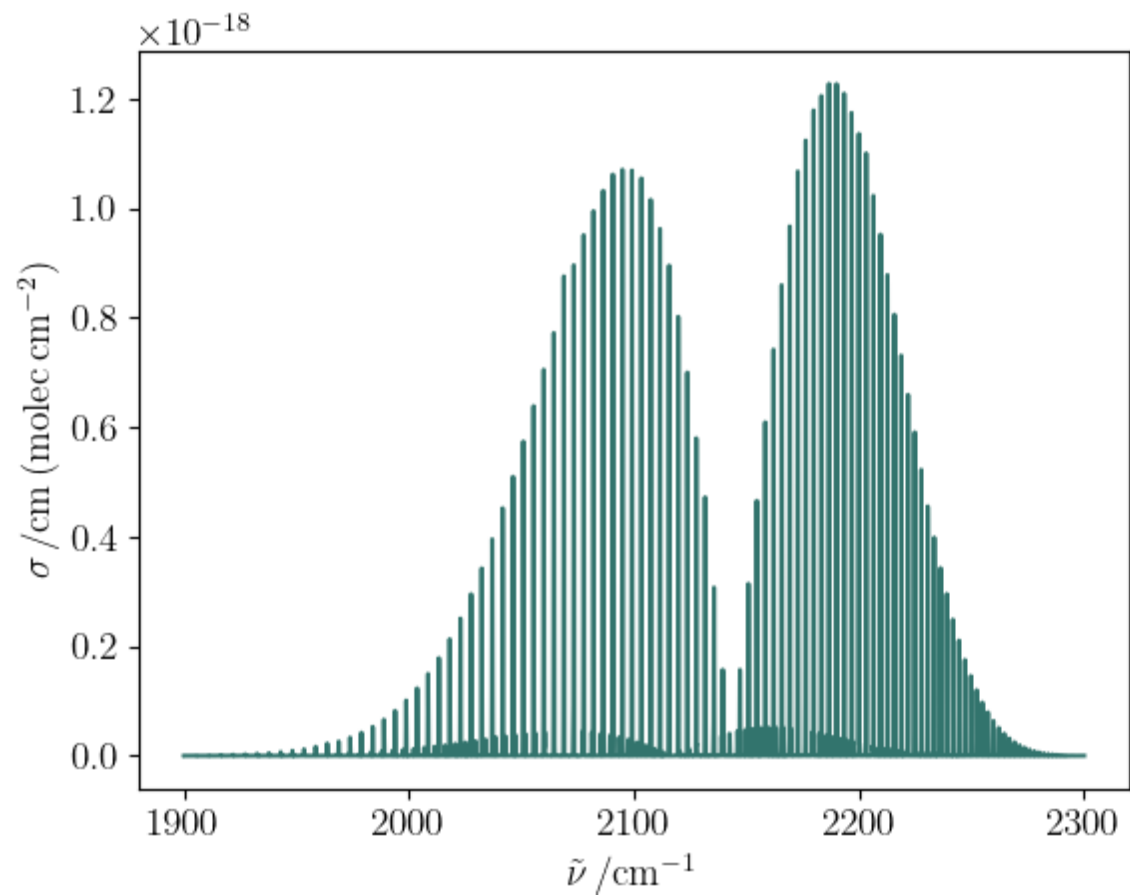
$$\left\langle \frac{1}{R^2} \right\rangle = \int_{-\infty}^{\infty} \psi_{\nu}^* \frac{1}{R^2} \psi_{\nu} \, dR$$

Vibration-Rotation Interaction



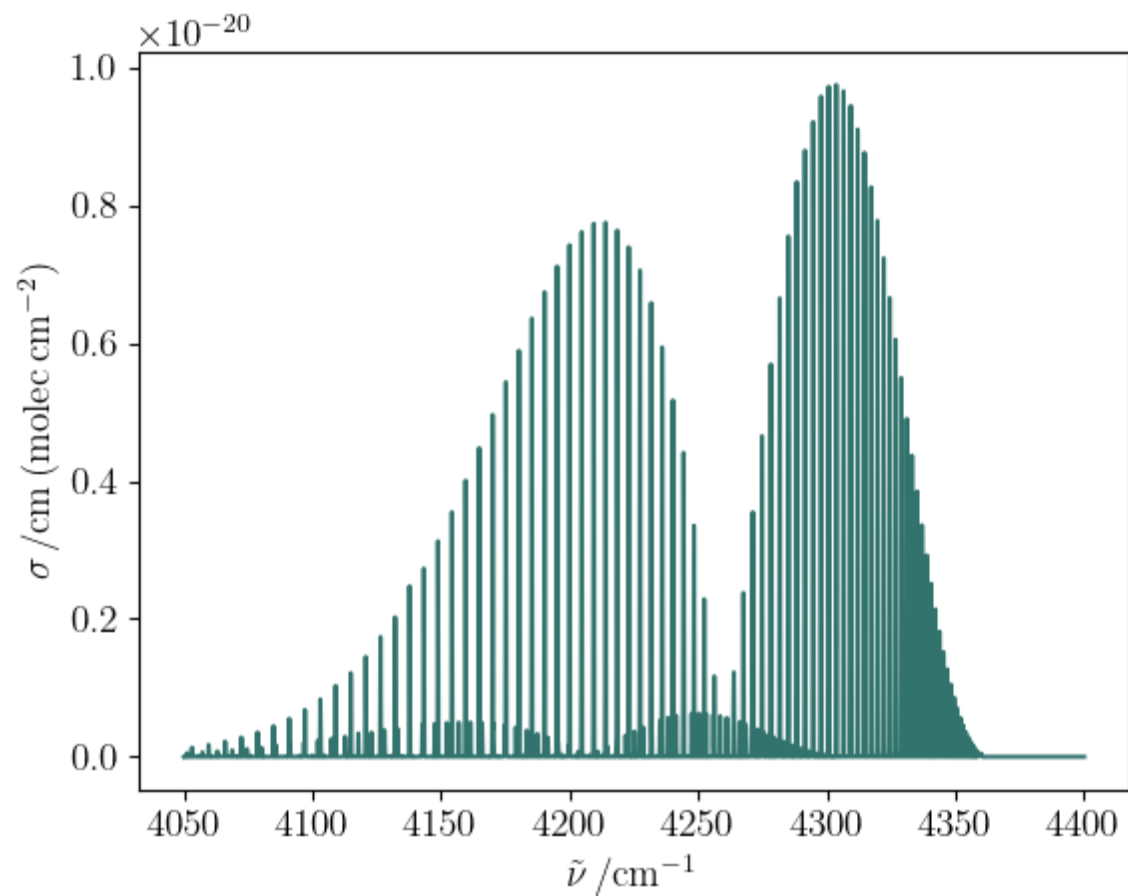
$$B_v = \frac{h}{8\pi^2 c \mu} \left\langle \frac{1}{R^2} \right\rangle = B_e - \alpha_e \left(v + \frac{1}{2} \right) + \gamma_e \left(v + \frac{1}{2} \right)^2 + \dots$$

Vibration-Rotation Interaction



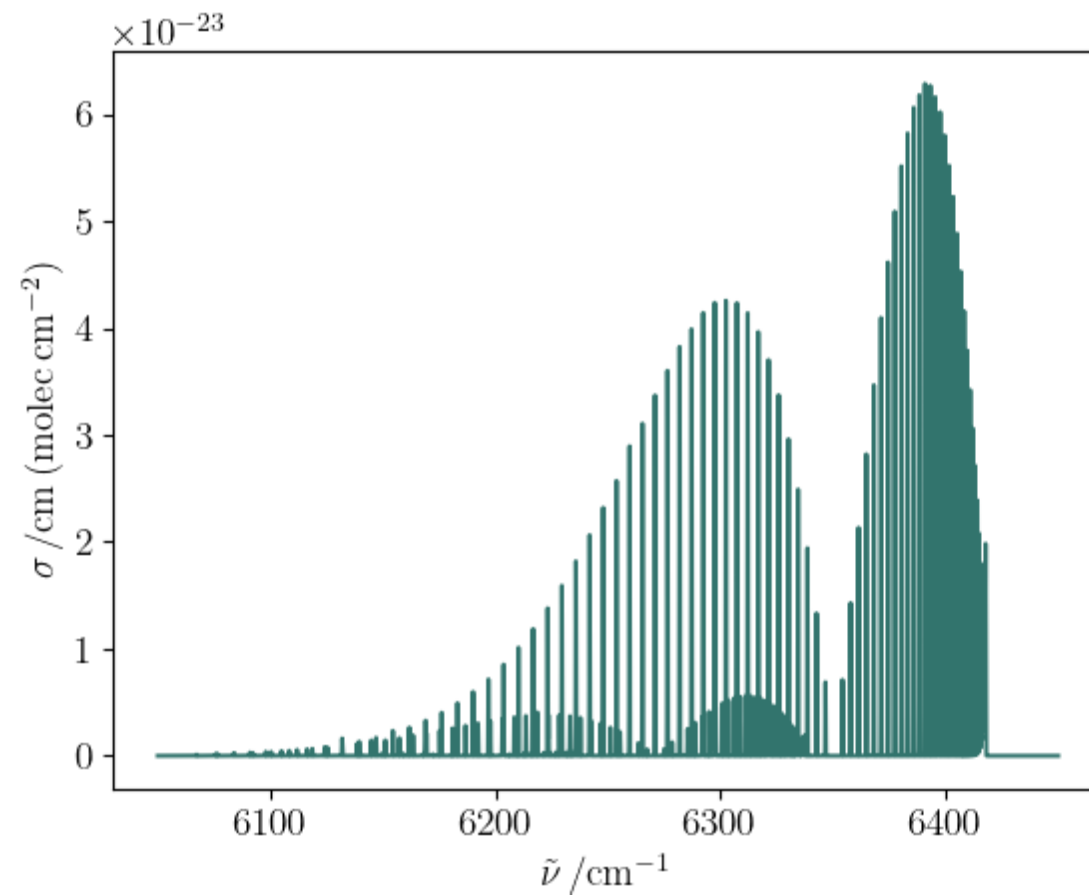
The 0-1 band of CO

Vibration-Rotation Interaction



The 0-2 band of CO

Vibration-Rotation Interaction



The 0-3 band of CO